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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>7</sup> :</b> B32B 27/08, C09J 151/00, 123/16	<b>A1</b>	<b>(11) International Publication Number:</b> WO 00/30849 <b>(43) International Publication Date:</b> 2 June 2000 (02.06.00)
<b>(21) International Application Number:</b> PCT/GB99/03499 <b>(22) International Filing Date:</b> 21 October 1999 (21.10.99)  <b>(30) Priority Data:</b> 9825721.5                      24 November 1998 (24.11.98)      GB  <b>(71) Applicant (for all designated States except US):</b> BP CHEMICALS LIMITED [GB/GB]; Britannic House, 1 Finsbury Circus, London EC2M 7BA (GB).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> BONNER, James, Graham [GB/GB]; 29 Connaught Place, Edinburgh EH6 4RQ (GB). GRAY, Alan [GB/GB]; 7 Annfield Grove, Stirling FK8 2BN (GB).  <b>(74) Agent:</b> COLLINS, Frances, Mary; BP International Limited, Patents & Agreements, Chertsey Road, Sunbury on Thames, Middlesex TW16 7LN (GB).		<b>(81) Designated States:</b> JP, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> A MULTI-LAYERED STRUCTURE  <b>(57) Abstract</b>  A multi-layer structure which comprises a first layer and a second layer, the first layer comprising a polyolefin composition or a polystyrene composition and the second layer comprising a polyketone composition, the first and second layers being bonded together with an intermediate layer of an adhesive composition which comprises a graft copolymer having a styrenic polymer backbone grafted with at least one polymerisable ethylenically unsaturated carboxylic acid or derivative thereof.		

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### A MULTI-LAYERED STRUCTURE

The present invention relates to multi-layered structures comprising at least one layer of an adhesive composition and at least one layer of a polyketone composition.

For the purposes of this patent, polyketones are defined as linear polymers having an alternating structure of (a) units derived from carbon monoxide and (b) units  
 5 derived from one or more olefinically unsaturated compounds. Although for the purposes of this patent polyketones correspond to this idealised structure, it is envisaged that materials corresponding to this structure in the main but containing small regimes (i.e. up to 10wt%) of the corresponding homopolymer or copolymer derived from the olefinically unsaturated compound, also fall within the definition.

10 Such polyketones have the formula:



where the R groups are independently hydrogen or hydrocarbyl groups, and m is a large integer; they are disclosed in several patents e.g. US 3694412. Processes for preparing  
 15 the polyketones are disclosed in US 3694412 and also in EP 181014 and EP 121965.

Adhesive compositions, also known as tie-layers or melt adhesives, are employed to bind together layers of materials which otherwise do not stick together satisfactorily. Polyolefin-containing blends suitable for use as adhesive layers in multi-layered structures are known. For example, US Patent 2081723 discloses a modified  
 20 polyolefin adhesive blend comprising (A) a graft copolymer of a polyethylene back-bone grafted with at least one polymerisable ethylenically unsaturated carboxylic acid or carboxylic acid anhydride and (B) a blending resin

mixture comprising a linear low density polyethylene and polypropylene. The patent states that the adhesive blends can be used to join polypropylene to a number of polar materials or to join two polar materials together.

WO 9509212 relates to a polyolefin-containing adhesive blend suitable for bonding polyolefins, in particular, polyethylene or polypropylene to polyketones which blend has good adhesion to polyolefins while maintaining good adhesion to the polyketone. The polyolefin-containing adhesive blend is said to comprise:

(A) 1 to 30 parts by weight of a graft copolymer having a polyolefin backbone grafted with 0.001 to 30% by weight of at least one polymerisable ethylenically unsaturated carboxylic acid or derivative thereof,

(B) 70 to 99 parts by weight of a polyolefin provided that at least 5 parts by weight of (B) is

(C) a polyolefin having a density of less than  $930\text{kgm}^{-3}$

wherein the graft copolymer (A) has been reacted with a compound (D) which has at least two primary or secondary amino groups at least one of which is a primary amino group, the sum of (A), (B) and (C) being 100 parts by weight.

There remains the need for further adhesive compositions which have good adhesion to polyketones and polyolefins or polystyrene.

We have discovered that certain compositions can successfully bind both polyolefins and polystyrene to polyketones.

Thus, the present invention provides a multi-layer structure which comprises a first layer and a second layer, the first layer comprising a polyolefin composition or a polystyrene composition and the second layer comprising a polyketone composition, the first and second layers being bonded together with an intermediate layer of an adhesive composition which comprises a graft copolymer having a styrenic polymer backbone grafted with at least one polymerisable ethylenically unsaturated carboxylic acid or derivative thereof.

The styrenic polymer used as the backbone of the graft copolymer can be a styrenic block copolymer. The term "styrenic block copolymer" is used to indicate a polymer characterised by at least one block of units derived from one or more vinyl aromatic hydrocarbons (A block) and at least one block of units derived from one or more olefins other than a vinyl aromatic hydrocarbon (B block). The vinyl aromatic

hydrocarbon useful as the precursor of A blocks has a vinyl group attached directly to an aromatic ring. Preferred vinyl aromatic compounds are styrene and substituted styrenes. Illustrative substituted styrenes include  $\alpha$ -methyl styrene,  $\alpha$ -ethylstyrene, p-methylstyrene, m-methylstyrene, p-ethylstyrene, m-isopropylstyrene, divinyl benzene,  $\alpha$ ,4-dimethylstyrene, chlorostyrene and vinyl benzene chloride. Olefins useful as precursors of the B blocks include ethylene, propylene, butylene, and dienes (e.g. isoprene, butadiene, 2,3-dimethylbutadiene, 1,3-octadiene, 1,3-pentadiene and norbornene). Preferably the styrenic block copolymer has the structure A-B-A. The block copolymer may be partially hydrogenated. Hydrogenation of block copolymers is well known in the art. Examples of styrenic block copolymers include styrene-ethylene/butylene-styrene block terpolymer (SEBS), styrene-butadiene-styrene block terpolymer (SBS) and styrene-isoprene-styrene block terpolymer (SIS). SEBS styrenic block copolymers are sold by Shell under the trade name of Kraton and by Asahi under the trade name of Tuftec.

Polymerisable ethylenically unsaturated carboxylic acids and derivatives thereof which are graft copolymerised with the styrenic polymer backbone include, for example, acrylic acid, methacrylic acid, maleic acid, itaconic acid, citraconic acid, mesaconic acid, maleic anhydride, 4-methyl cyclohex-4-ene-1,2-dicarboxylic acid anhydride, bicyclo (2.2.2) oct-5-ene-2,3-dicarboxylic acid anhydride, 1,2,3,4,5,8,9,10-octahydronaphthalene-2,3 dicarboxylic acid anhydride, 2-oxa-1,3-diketospiro (4.4) non-7-ene, bicyclo (2.2.1) hept-5-ene-2,3-dicarboxylic acid anhydride, maleopimaric acid, tetrahydrophthalic anhydride, x-methyl-bicyclo (2.2.1) hept-5-ene -2,3-dicarboxylic acid anhydride, x-methyl-norborn-5-ene-2, dicarboxylic acid anhydride, norborn-5-ene-2,3-dicarboxylic acid anhydride. Preferably, maleic anhydride is used. When maleic anhydride is used as the polymerisable ethylenically unsaturated carboxylic acid anhydride, the amount which is graft copolymerised with the styrenic polymer backbone is typically from 0.001 to 5%, preferably from 0.05 to 3% more preferably from 0.5 to 2 % by weight of the graft copolymer.

The adhesive composition may comprise a mixture of two or more of the graft copolymers.

Methods for preparing graft copolymers are well known and any suitable method can be used to prepare the graft copolymer of the styrenic polymer and the

polymerisable ethylenically unsaturated carboxylic acid or derivative thereof. One such suitable method comprises blending together the styrenic polymer and the polymerisable ethylenically unsaturated carboxylic acid or derivative thereof in the presence of a free radical initiator, such as an organic peroxide or hydroperoxide, at a temperature which is  
5 above the melting point of the styrenic polymer and which provides a suitable half-life of the free radical initiator. Suitable free radical initiators are well known. This grafting process can be carried out using known mixing equipment such as, for example, a Brabender mixer, a Banbury mixer or a roll mill. Preferably, the grafting process is carried out in a closed vessel. A convenient method of preparing the graft copolymer is  
10 therefore to extrude the styrenic polymer which forms the polymer backbone, the polymerisable ethylenically unsaturated carboxylic acid or derivative thereof and an organic peroxide or hydroperoxide through a single or multiple screw extruder. Alternatively, the styrenic polymer may be dissolved or suspended in a solvent and the resulting solution or suspension is mixed with the polymerisable ethylenically unsaturated  
15 carboxylic acid or derivative thereof and the free radical initiator.

Optionally, the graft copolymer may be further reacted with a compound (A) which has (a) a primary amino group and (b) at least one further group selected from the group consisting of a primary amino group, a secondary amino group and a hydroxyl group.

20 It is preferred that compound (A) is a diamine having two primary amino groups and up to 16 carbon atoms inclusive and at least two carbon atoms between the primary amino groups. The diamines suitably contain aromatic moieties linking the amino groups as illustrated by phenylenediamine, 4,4'-diaminobiphenyl and di(4-aminophenyl) ether, or the diamines contain cycloaliphatic linking moieties such as in the  
25 case of di(4-aminocyclohexyl)methane or 1,4-diaminocyclooctane. The preferred diamines, however, are the acyclic terminal primary diamines of the formula:



wherein n is an integer from 2 to 16 inclusive. Such polymethylenediamines include trimethylenediamine, tetramethylenediamine, hexamethylenediamine,  
30 decamethylenediamine, dodecamethylenediamine and hexadecamethylenediamine. Of these diamines dodecamethylenediamine is preferred.

Compound (A) which is optionally reacted with the graft copolymer can also



suitably be a polyalkylene polyamine, or a mixture thereof, having the formula:-



wherein R is a divalent aliphatic hydrocarbon group having 2 to 4 carbon atoms and n is an integer in the range from 1 to 10. More preferably the amine is a polyalkylene polyamine of the formula (II) wherein R is the group  $-\text{CH}_2\text{CH}_2-$  and n has a value of 2 to 6, i.e. a polyethylene polyamine. Examples of suitable polyethylene polyamines include triethylene tetramine and tetraethylene pentamine.

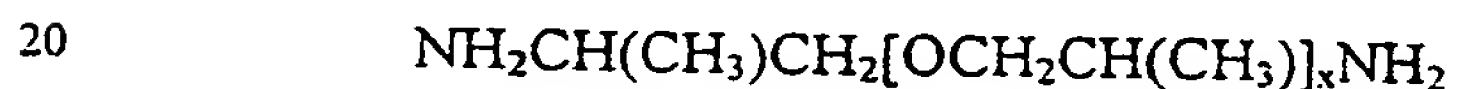
Hydroxyalkyl amines, for example ethanolamine, diethanolamine, 2-hydroxypropylamine and N-hydroxy-ethyl ethylenediamines, and the like may also be used as the compound (A).

Furthermore, compound (A) can be a compound of formula (III),



wherein one of  $\text{R}^1$  and  $\text{R}^2$  is hydrogen and the other is hydrogen or lower alkyl, preferably  $\text{C}_2$ - $\text{C}_6$  alkyl, more preferably methyl, and n is an integer from 1 to 40, preferably 1 to 10, more preferably 1 to 7, for example 2 to 7, one of  $\text{R}^3$  and  $\text{R}^4$  is hydrogen and the other is hydrogen or lower alkyl, preferably  $\text{C}_2$ - $\text{C}_6$  alkyl, more preferably methyl.

In particular where the compound (A) is of formula (III) it is preferred that compounds of formula,



where  $x = 33.1, 5.6$  and  $2.6$  are used. These compounds are commercially available and are marketed under the trade names Jeffamine D2,000, D400 and D230 respectively.

The amount of compound (A) which is optionally reacted with the graft copolymer is from 0.01 to 2.0%, preferably from 0.05 to 1.0% by weight of the resulting amine functionalised graft copolymer. The optimum amount of compound (A) varies depending on the graft copolymer.

Compound (A) can be reacted with the graft copolymer in several ways; a preferred method is to react the graft copolymer and compound (A) in the melt by melt mixing them in known mixing equipment e.g. a Brabender mixer, a Banbury mixer or a roll mill or twin screw extruder. It is also possible to melt mix the diamine with the graft copolymer in the grafting process itself preferably in two steps.

Optionally, a polyolefin is added to the adhesive composition to modify the



rheological, viscoelastic or adhesive properties of the composition ("modifying polyolefin"). Any suitable polyolefin can be used e.g. polyethylene, polypropylene, copolymers of ethylene or copolymers of propylene with one or more comonomers e.g. butylene. Suitably, the modifying polyolefin may be a very low density polyethylene (VLDPE), linear low density polyethylene (LLDPE) or ethylene propylene rubbers, preferably VLDPE. A mixture of two or more modifying polyolefins can be added to the adhesive composition.

Where a modifying polyolefin is added to the adhesive composition, the modifying polyolefin is present in amounts of from 40 to 80% by weight, preferably 50 to 70% by weight based on the total amount of the adhesive composition.

Particularly preferred graft copolymers include a SEBS block terpolymer grafted with maleic anhydride and subsequently reacted with compound (A) as well as blends of VLDPE and such amine modified SEBS block terpolymers.

The adhesive composition may optionally comprise a polyketone. It is preferred that the optional polyketone is the same as the polyketone of the second layer.

Where a polyketone is present in the adhesive composition it is preferred that the polyketone is present in the adhesive composition in amounts in the range 10 to 50% by weight, more preferably 20 to 40% by weight based on the total weight of the polymers of adhesive composition.

The graft copolymer, the optional modifying polyolefin and the optional polyketone can be blended using known techniques and equipment for batch or continuous blending.

The adhesive composition may also contain conventional additives such as, for example, antioxidants, stabilisers, processing aids, fillers and mould release agents.

Methods for using adhesive compositions to bond polyolefins or polystyrenes to polar substrates are known and include lamination, coextrusion, extrusion lamination and coextrusion coating. In particular, the present invention relates to multi-layered structures when prepared by co-extrusion e.g. multi-layered film produced by co-extrusion.

Where the first layer comprises a polyolefin composition, the polyolefin composition may comprise a polyolefin, blends of polyolefins or blends of a polyolefin and a polymer other than a polyolefin (for example, a blend of a polyolefin and a

polyamide). Preferably, the polyolefin composition of the first layer comprises a major proportion of a polyolefin. The polyolefin composition of the first layer may comprise a recycled polyolefin or a mixture of recycled and virgin polyolefin. The polyolefin composition of the first layer may contain conventional fillers. Suitable polyolefins include a homopolymer of an olefin e.g. ethylene or propylene, in particular polypropylene, a high density polyethylene (HDPE), a low density polyethylene (LDPE), a linear low density polyethylene (LLDPE) or a very low density polyethylene (VLDPE), preferably polypropylene, HDPE or LLDPE. Alternatively, the polyolefin may be a copolymer of an olefin e.g. propylene with ethylene, butylene or other unsaturated aliphatic hydrocarbons or a terpolymer of an olefin e.g. ethylene with propylene and a diene. Blends of two or more polyolefins can be used.

Where the first layer comprises a polystyrene composition, the polystyrene composition may comprise a crystal polystyrene or a high impact polystyrene (HIPS).

High-impact polystyrene is typically styrene that has been polymerised in the presence of a rubber modifier, for example, butadiene to give polystyrene with particles of the rubber modifier dispersed in the polymer matrix. Where polybutadiene is used in this way, it typically constitutes 3-10% by weight of the high impact polystyrene. The polystyrene may contain up to 20% by weight of a comonomer, for example, maleic anhydride, butadiene or acrylonitrile. Typical of polystyrene with maleic anhydride comonomer are Dylark (ex Nova Chemicals) and SMA (ex DSM) resins.

Where the polystyrene is a crystal polystyrene, the weight average molecular weight is preferably in the range 150,000 to 400,000 more preferably 220,000 to 320,000. Where the polystyrene is a high-impact polystyrene, the weight average molecular weight is preferably in the range 180,000 to 220,000 for example 190,000 to 210,000.

The polystyrene composition of the first layer may comprise a blend of a polyketone and a polystyrene as described in EP 0839866. Preferably, the polyketone which is blended with the polystyrene is the same as the polyketone used in the polyketone composition of the second layer.

The polyketone composition of the second layer comprises a linear polymer having an alternating structure of (a) units derived from carbon monoxide and (b) units derived from one or more olefinically unsaturated compounds. Suitable olefinic units are

those derived from C<sub>2</sub> to C<sub>12</sub> alpha-olefins or substituted derivatives thereof or styrene or alkyl substituted derivatives of styrene. It is preferred that such olefin or olefins are selected from C<sub>2</sub> to C<sub>6</sub> normal alpha-olefins (i.e. straight chain alpha-olefins) and it is particularly preferred that the olefin units are either derived from ethylene or most preferred of all from a mixture of ethylene and one or more C<sub>3</sub> to C<sub>6</sub> normal alpha-olefin(s) especially propylene or butylene (i.e. an ethylene/propylene/CO terpolymer or an ethylene/butylene/CO terpolymer). In these most preferable materials it is further preferred that the molar ratio of ethylene units to C<sub>3</sub> to C<sub>6</sub> normal alpha-olefin units is greater than or equal to 1 most preferably between 2 and 30. The polyketone composition of the second layer may comprise blends of polyketones or blends of polyketones and a polymer other than a polyketone (for example, polystyrene, polyamides, HDPE, LLDPE, LDPE or polypropylene).

The polyketones employed in the invention preferably have a number average molecular weight of from 20000 to 500,000, preferably from 15,000 to 300,000, more preferably from 40,000 to 200,000 as determined by gel permeation chromatography.

The melting point of the polyketones is preferably between 175 and 300°C, preferably from 180 to 225°C.

The multi-layered structures according to the present invention can include further layers in addition to the three layers hereinbefore defined. For example, a five-layered structure can comprise a first layer of a polyolefin composition or a polystyrene composition, a second layer of an adhesive composition as defined above, a third layer of a polyketone composition, a fourth layer of an adhesive composition as defined above and a fifth layer of a polyolefin composition or a polystyrene composition.

It has been found that the use of the adhesive compositions defined above to produce multi-layered film or sheet provides a satisfactory bond when the film or sheet is subsequently thermoformed, i.e. the film or sheet does not have a tendency to delaminate after thermoforming into articles e.g. into receptacles (containers). The present invention includes film, sheet and articles (e.g. receptacles, pipe or tubing) having the multi-layered structure of the present invention.

The invention is illustrated by the following examples:

#### Determination of Melt Flow Rate

The melt flow rate (MFR) of the polyketone (PK) was measured using a

Davenport Melt Index Tester. Tests were carried out at a temperature of 250°C and an applied load of 5 kg. The MFR was calculated from the mass of extrudate pushed through a die (2.095 mm diameter) over a 30 second period on application of the load 4 minutes after charging the polymer into the barrel of the instrument at a temperature of 250°C. Otherwise, standard MFR procedures were followed (e.g. ISO 1133). The melt flow rates (MFR) of the polyethylenes, polypropylene and polystyrene were measured under the same conditions.

#### Preparation of three-layer sandwich

A three-layer sandwich comprising a layer of each of the materials to be bonded separated by a layer of the tie-layer material was prepared. Each layer was 130µm thick. The three layers were positioned in a mould 360µm thick which was then placed in a press at 240°C. After a 30-second preheat the sandwich was compression moulded under a load of 10 tons for 10 seconds, and then crash cooled to room temperature. The level of adhesion between the layers was then assessed.

#### Materials

Details of the materials to be bonded and those used as tie-layers are given in the tables below:

**TABLE 1 - materials to be bonded (first layer)**

MATERIAL	GRADE/ NAME	MFR	DENSITY (kg/m <sup>3</sup> )	SUPPLIER
Polyethylene (HDPE)	HD5502XA	0.2	955	BP Chemicals
Polystyrene	HIPS 5400	2	1050	BP Chemicals

**TABLE 2 - materials to be bonded (second layer)**

MATERIAL	T <sub>m</sub> (°C)	MFR
Ethylene/propylene/CO terpolymer	200	70

TABLE 3 - materials used in the preparation of the tie-layers

MATERIAL	NAME	SUPPLIER
VLDPE	Clearflex MQFO	Enichem
SEBS-g-MAH	Kraton FG1901X	Shell
SEBS-g-MAH	Tuftec M1962	Asahi

EXAMPLE 1 - Tie-layers for polyketone and polyethylene or polystyrene

A tie-layer comprising a 50:50 w/w mix of Kraton FG1901X and Clearflex MQFO was prepared using a ZSK30 co-rotating twin screw extruder. The extruder was operated using a screw speed of 100 rpm, a temperature profile zone 1 = 180°C, zones 2-5 = 200°C, and a nominal output of 7 kg/hour.

The tie layer were compression moulded as described previously into three-layer sandwiches between polyketone and polyethylene or polystyrene. The degree of adhesion was tested by simply evaluating subjectively the degree of adhesion of the two layers, and the ease with which they could be peeled apart.

Results of the adhesion evaluations on the tie-layer are given in Table 4 below.

TABLE 4

TIE-LAYER COMPONENTS (50:50 w/w)	ADHESION RATING POLYKETONE*	ADHESION RATING POLYETHYLENE*	ADHESION RATING POLYSTYRENE*
Kraton FG1901X / Clearflex MQFO	2(3)	2(3)	2(3)

\*Ratings as follows:

- 0 - no adhesion
- 1 - low level of adhesion and sample could be peeled apart
- 2 - high level of adhesion, but sample could still be peeled apart
- 3 - adhesion level so high that sample could not be peeled.

The above results show that the tie-layer has good adhesion to polyketone, polyethylene and polystyrene.

EXAMPLE 2 - Tie-layers for polyketone and polyethylene or polystyrene

A tie-layer comprising an amine functionalised SEBS polymer (SEBS-NH<sub>2</sub>) was prepared by reacting Tuftec M1962 (SEBS-g-MAH) with 1,12-diaminododecane (DADD) as follows: Tuftec M1962 was cryoground in a Fritsch grinder to a fine powder and was then  
5 dried at a temperature of 50°C for a period of 2 hours under vacuum. The dried material was then mixed with 1% w/w of DADD and the resulting mixture was compounded using a Prism 16mm twin screw corotating extruder. The temperature profile of the extruder as 180, 200 and 210°C along the feed, barrel and die sections of the extruder respectively. The screw speed was 150 rpm and the torque was 40%.

10 The tie layer was compression moulded as described previously into three-layer sandwiches between polyketone and polyethylene or polystyrene. The degree of adhesion was tested by simply evaluating subjectively the degree of adhesion of the two layers, and the ease with which they could be peeled apart.

Results of the adhesion evaluations on the tie-layer are given in Table 5 below.

TABLE 5

TIE-LAYER COMPONENTS	ADHESION RATING POLYKETONE*	ADHESION RATING POLYETHYLENE*	ADHESION RATING POLYSTYRENE*
SEBS-NH <sub>2</sub>	3	3	3

\*Ratings as follows:

0 - no adhesion

1 - low level of adhesion and sample could be peeled apart

2 - high level of adhesion, but sample could still be peeled apart

20 3 - adhesion level so high that sample could not be peeled.



Claims

1. A multi-layer structure which comprises a first layer and a second layer, the first layer comprising a polyolefin composition or a polystyrene composition and the second layer comprising a polyketone composition, the first and second layers being bonded together with an intermediate layer of an adhesive composition which comprises  
5 a graft copolymer having a styrenic polymer backbone grafted with at least one polymerisable ethylenically unsaturated carboxylic acid or derivative thereof.
2. A multi-layered structure as claimed in claim 1 wherein the polyketone composition of the second layer comprises a linear polyketone polymer having an alternating structure of (a) units derived from carbon monoxide and (b) units derived  
10 from one or more olefinically unsaturated compounds.
3. A multi-layered structure as claimed in claim 2 wherein the polyketone composition of the second layer comprises an ethylene/propylene/CO terpolymer or an ethylene/butylene/CO terpolymer.
4. A multi-layered structure as claimed in any one of the preceding claims wherein  
15 the adhesive composition comprises a graft copolymer having a backbone derived from a styrenic block copolymer.
5. A multi-layered structure as claimed in claim 4 wherein the styrenic block copolymer is selected from the group consisting of styrene-ethylene/butylene-styrene block terpolymers (SEBS), styrene-butadiene-styrene block terpolymers (SBS) and  
20 styrene-isoprene-styrene block terpolymers (SIS).
6. A multi-layered structure as claimed in any one of the preceding claims wherein the graft copolymer of the adhesive composition is grafted with 0.001 to 5% by weight



of maleic anhydride.

7. A multi-layered structure as claimed in any one of the preceding claims wherein the graft copolymer of the adhesive composition has been reacted with a compound (A) which has (a) a primary amino group and (b) at least one further group selected from the group consisting of a primary amino group, a secondary amino group and a hydroxyl group.

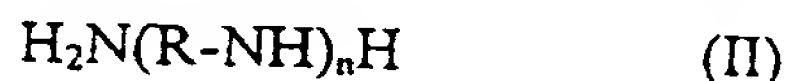
8. A multi-layered structure as claimed in claim 7 wherein the compound (A) is selected from the group consisting of:

(a) acyclic terminal primary diamines of the formula:



wherein n is an integer from 2 to 16 inclusive;

(b) polyalkylene polyamines having the formula:



wherein R is a divalent aliphatic hydrocarbon group having 2 to 4 carbon atoms and n is an integer in the range from 1 to 10;

(c) hydroxyalkyl amines; and

(d) compounds of the formula (III),



wherein one of  $\text{R}^1$  and  $\text{R}^2$  is hydrogen and the other is hydrogen or lower alkyl, and n is an integer from 1 to 40.

9. A multi-layered structure as claimed in claims 7 or 8 wherein the amount of compound (A) which has been reacted with the graft copolymer is from 0.01 to 2.0% by weight of the resulting amine functionalised graft copolymer.

10. A multi-layered structure as claimed in any one of the preceding claims wherein the adhesive composition additionally comprises a modifying polyolefin selected from the group consisting of very low density polyethylene (VLDPE), linear low density polyethylene (LLDPE) and ethylene propylene rubbers.

11. A multi-layered structure as claimed in claim 10 wherein the modifying polyolefin is present in the adhesive composition in an amount of from 40 to 80% by weight based on the total amount of the adhesive composition.

12. A multi-layered structure as claimed in claims 10 or 11 wherein the adhesive composition additionally comprises a polyketone in an amount in the range 10 to 50% by

weight based on the total weight of the polymers of adhesive composition.

13. A multi-layered structure as claimed in any one of the preceding claims wherein the first layer comprises a polyolefin composition comprising a polyolefin selected from the group consisting of high density polyethylene (HDPE), low density polyethylene (LDPE), linear low density polyethylene (LLDPE), very low density polyethylene (VLDPE), polypropylene, copolymers of propylene with ethylene or butylene and terpolymers of ethylene with propylene and a diene.

14. A multi-layered structure as claimed in any one of claims 1 to 12 wherein the first layer comprises a polystyrene composition comprising a crystal polystyrene or a high impact polystyrene.

15. Film, sheet, pipe or tubing comprising a multi-layered structure as defined in any one of the preceding claims.

16. An article obtainable by thermoforming a multi-layered film or sheet as claimed in claim 15.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 99/03499

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B32B27/08 C09J151/00 C09J123/16

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B32B C09J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	WO 99 43496 A (BONNER JAMES GRAHAM ; BP CHEM INT LTD (GB); POWELL ANTHONY KEITH (G) 2 September 1999 (1999-09-02) page 3, line 32 -page 4, line 16; claims page 6, line 34 -page 7, line 9 page 7, line 32 -page 9, line 15 ---	1-5, 10-13, 15, 16
A	WO 95 09212 A (BP CHEM INT LTD ; BONNER JAMES GRAHAM (GB); HODGSON PHILIP KENNETH) 6 April 1995 (1995-04-06) cited in the application page 6, line 7 - line 32; claims; examples page 8, line 24 - line 34 ---	1-16
A	EP 0 389 094 A (MORTON INT INC) 26 September 1990 (1990-09-26)  page 2, line 3 - line 5; claims -----	1, 4-6, 10, 11, 13, 15, 16

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

20 January 2000

Date of mailing of the international search report

02/02/2000

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# INTERNATIONAL SEARCH REPORT

information on patent family members

Inter 1st Application No

PCT/GB 99/03499

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
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